DET NORSKE VERITAS

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Technical and Economic Feasibility of Preventing SCC Through Control of Oxygen

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Technical and Economic Feasibility of Preventing SCC through Control of Oxygen	DET NORSKE VERITAS (U.S.A.), INC. Materials & Corrosion Technology Center 5777 Frantz Road Dublin, OH 43017-1386, United States Tel: (614) 761-1214 Fax: (614) 761-1633 http://www.dnv.com http://www.dnvcolumbus.com
For: Pipeline & Hazardous Materials Safety Administration U.S. Department of Transportation East Building, 2nd Floor 1200 New Jersey Ave., SE Washington, DC 20590	
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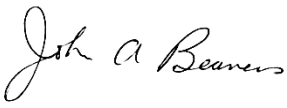
See Executive Summary

Prepared by:	Feng Gui, Ph.D. Senior Engineer	*Signature* 
Verified by:	John A. Beavers, Ph.D., FNACE Director – Failure Analysis	*Signature* 
Approved by:	Narasi Sridhar, Ph.D. Director – Program Director Materials and Sensors Program	*Signature* 

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Executive Summary

Stress corrosion cracking (SCC) has been observed in carbon steel tanks and piping in contact with fuel grade ethanol (FGE) in user terminals, storage tanks, and loading/unloading racks. Detailed laboratory studies, sponsored by American Petroleum Institute (API), Renewable Fuel Association (RFA), Pipeline Research Council International (PRCI), and Pipeline and Hazardous Materials and Safety Administration (PHMSA), demonstrated that, in ASTM D-4806 FGE, dissolved oxygen was the most important factor leading to SCC, followed in importance by pre-existing scale on the steel, chloride, and methanol. In a Roadmapping Workshop conducted in October 2007, methods to avoid oxygen contamination in ethanol and defining safe operating limits in terms of ethanol chemistry and oxygen concentration were identified as major gaps in the safe transportation of ethanol in pipelines.

Through the research programs listed above, it has been consistently observed that SCC can be prevented by eliminating oxygen from FGE, independent of the ethanol and gasoline blending ratios. The measures that have been explored to remove oxygen from FGE include adding chemical oxygen scavengers, sparging FGE with an inert gas (e.g. nitrogen or argon), vacuum treatment and reacting with steel wool. However, most of these oxygen removal methods have only been evaluated in laboratory tests in static liquids. Furthermore, some oxygen removal methods, such as the use of chemical oxygen scavengers, have not been evaluated extensively under conditions similar to those encountered in the field. Thus, even though the laboratory results suggest it is plausible to employ these methods to remove oxygen and hence to control SCC, it is uncertain whether they are feasible from engineering and economic perspectives in actual ethanol pipeline operation. Additionally, the existing technology is not capable of measuring oxygen concentration directly in FGE. Thus, it is useful to have a direct and rapid method for oxygen measurement so that the SCC potency of FGE in storage tanks and/or pipelines can be assessed

The objectives of the project were:

- Evaluate the performance and efficacy of oxygen scavengers under flowing conditions;
- Develop a model to calculate the oxygen consumption in the pipeline under flowing conditions;
- Develop a system that can provide rapid and direct oxygen concentration measurement;
- Perform an engineering and economic feasibility evaluation of preventing SCC by the control of oxygen and provide recommendations;

The following tests were performed to achieve the above objectives:

- Slow strain tests under flowing condition to evaluate oxygen scavenger performance;
- A crack growth rate test to evaluate oxygen scavenger performance;
- A flow loop test to evaluate oxygen removal feasibility and the direct oxygen measurement system;
- Long term immersion tests to determine the corrosion rate of carbon steel in FGE under different aeration conditions
- Vapor pressure measurements to provide data for a direct oxygen measurement system

Based on the performed tests, these are the key results:

- Isoascorbic acid and hydrazine showed promising performance in preventing SCC of carbon steel in FGE by consuming oxygen. The results suggest the critical dissolved oxygen concentration for SCC to occur could be at or higher than 40 ppm (10% volume in gas phase). Hydrazine, however, was not selected as the recommended scavenger due to its toxic nature;
- The performance of the oxygen scavenger, isoascorbic acid, was confirmed in a flow loop test. While it is efficient in decreasing the dissolved oxygen concentration from an initial level of 40 ppm to below 10 ppm, it can take a long time to decrease the oxygen concentration from an initial level of 80 ppm to below 40 ppm;
- A direct oxygen measurement system was developed that can provide the direct oxygen concentration level in FGE. The system accounts for the vapor pressure of FGE and has the equation for converting `oxygen partial pressure to concentration reading embedded. The lab evaluation and the flow loop testing both confirmed its performance;
- Oxygen consumption by corrosion was proved to be minimal. Thus, measures need to be taken in pipeline operation to avoid oxygen uptake during transmission.
- The comprehensive evaluation of the oxygen control methods taking into consideration of technical feasibility, cost, field implementation feasibility, and corrosion suggest oxygen control may not be an attractive method to prevent SCC for large volumes of FGE; for small volumes of FGE with proper agitation, nitrogen deaeration could be an option since it does not require the addition of chemicals and thus will not cause concerns over downstream materials compatibility;

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1.0 BACKGROUND

Ethanol has attracted much attention in recent years as an alternative fuel source in an effort to improve security of supply and energy independence. In the US, the US Department of Energy (DOE) calls for 30% of today's fuel use to be supplanted by 2030 with alternate fuels, including ethanol[1]. Worldwide, ethanol demand is expected to more than double in the next ten years[2]. Although most of the ethanol is currently transported by tanker trucks, rail cars, and barges, pipelines are still the most efficient system to transport ethanol. Thus, with increases in ethanol demand, it is expected that pipelines - both the existing pipeline infrastructure and new pipeline construction - will play a major role in transporting ethanol.

Stress corrosion cracking (SCC) has been observed in carbon steel tanks and piping in contact with fuel grade ethanol (FGE) in user terminals, storage tanks, and loading/unloading racks. Detailed laboratory studies[3], sponsored by American Petroleum Institute (API), Renewable Fuel Association (RFA), Pipeline Research Council International (PRCI), and Pipeline and Hazardous Materials and Safety Administration (PHMSA), demonstrated that, in ASTM D-4806 FGE, dissolved oxygen was the most important factor leading to SCC, followed in importance by pre-existing scale on steel, chloride, and methanol. In a Roadmapping Workshop conducted in October 2007[4], methods to avoid oxygen contamination in ethanol and defining safe operating limits in terms of ethanol chemistry and oxygen concentration were identified as major gaps in the safe transportation of ethanol in pipelines.

Through the research programs listed above, it has been consistently observed that SCC can be prevented by eliminating oxygen from FGE, independent of the ethanol and gasoline blending ratios. The measures that have been explored to remove oxygen from FGE include adding chemical oxygen scavengers, sparging FGE with an inert gas (e.g. nitrogen or argon), vacuum treatment and reacting with steel wool. However, most of these oxygen removal methods have only been evaluated in laboratory tests in static liquids. Furthermore, some oxygen removal methods, such as the use of chemical oxygen scavengers, have not been evaluated extensively under conditions similar to those encountered in the field. Thus, even though the laboratory results suggest it is plausible to employ these methods to remove oxygen and hence to control SCC, it is uncertain whether they are feasible from engineering and economic perspectives in actual ethanol pipeline operation. Additionally, the existing technology is not capable of measuring oxygen concentration directly in FGE. Thus, it is essential to have a direct and rapid

1 C. Schubert, Nature Biotechnology, 24, 777 (2006).
2 M. F. Demirbas and M. Balat, Energy Conversion and Management, 47, 2371 (2006).
3 N. Sridhar, K. Price, J. Buckingham and J. Dante, "Stress Corrosion Cracking of Carbon Steel in Ethanol", Corrosion, v62, 8 (2006):p687
4 Safe & Reliable Ethanol Transportation & Stroage Technology Roadmapping Workshop, October 25-27, 2007, Dublin, OH, Report prepared by DNV Columbus and Energetics.

method for oxygen measurement so that the susceptibility of storage tanks and/or pipelines to SCC can be well understood.

2.0 OBJECTIVES

The major objectives of the proposed project were to:

1. Evaluate the performance and efficacy of oxygen scavengers under flowing conditions;
2. Develop a model to calculate the oxygen consumption in the pipeline under flowing conditions;
3. Develop a system that can provide rapid and direct oxygen concentration measurement;
4. Perform an engineering and economic feasibility evaluation of preventing SCC by the control of oxygen and provide recommendations;

3.0 PROJECT SCOPE

To achieve the objectives of the projects, the following tests were performed:

- slow strain tests under flowing condition to evaluate oxygen scavenger performance;
- crack growth rate test to evaluate oxygen scavenger performance;
- flow loop test to evaluate oxygen removal feasibility and the direct oxygen measurement system;
- long term immersion tests to obtain the corrosion of carbon steel in fuel grade ethanol under different aeration conditions
- vapor pressure measurement to provide data for direct oxygen measurement system

The results from these efforts are summarized below.

4.0 EXPERIMENTAL APPROACH

4.1 Slow Strain Tests Under Flowing Condition

Slow strain rate (SSR) tests were performed under flowing conditions to evaluate the performance of oxygen scavengers. All SSR tests were performed with samples machined out of

a segment of 40 inch diameter X 0.344 inch wall thickness API 5L X60 line pipe. The chemical composition of the line pipe steel is given in Table 1 and the mechanical properties are given in Tables 2 and 3. The testing was performed using a simulated FGE (SFGE) containing 5 ppm Cl. The additives used to prepare the SFGE are shown in Table 4 and the target composition is shown in Table 5.

4.2 Scaling up Flow Effects

In order to evaluate the effect of fluid flow on corrosion/SCC in a pipeline, the laboratory flow experiments should simulate the hydrodynamics of the pipeline adequately. Wall shear stress has been used as a method of scaling up laboratory tests to actual pipe flow [7-9]. Wall shear stress is a measure of momentum transfer between the fluid and the wall of the pipe or corroding metal. The assumption here is that, if the wall shear stress in the laboratory test conditions is the same as the wall shear stress in the pipeline, then the laboratory test conditions simulate the mechanism of corrosion in the actual application (a pipeline carrying ethanol) adequately. It must be noted that, since our interest is simulating the environmental conditions leading to SCC, the use of wall shear stress does not completely consider the effect of cracks. However, because we are interested in the electrochemical conditions leading to SCC, the effect of flow on the smooth surfaces of the specimen are of greater interest than the flow at the crack tip.

For Tube /Pipe Flow, wall shear stress is calculated as follows:

$$\tau_w = \left(\frac{f \rho V^2}{2} \right) \tag{1}$$

τ_w = wall shear stress, Pa
f = friction factor
ρ = density, kg/m^3
V = velocity, m/s

The friction factor is related to the Reynolds number, Re, through a number of empirical equations [8]. For pipe flow, the Blasius equation is used:

$$f = 0.0791 \times \mathrm{Re}^{-0.25} \tag{2}$$

Where, Re is given by

$$\mathrm{Re} = \frac{\rho V d}{\mu} \tag{3}$$

μ = absolute viscosity, kg/m.s
d = pipe diameter, m

Combining Eq. 1 through 3, we obtain

$$\tau_w = 0.0792 \times \left(\frac{d}{2\mu}\right)^{-0.25} \times \rho^{0.75} \times V^{1.75} \quad (4)$$

Using Eq. 4, the wall shear stress for pipe and the tubing system used for the laboratory test is compared in Table 1.

From Table 1, for example, to achieve the equivalent corrosion/electrochemical behavior of a 12-inch pipe flowing ethanol at 2 m/s, the laboratory flow loop has to flow the ethanol at 1.1 m/s.

4.3 Test Procedures

The specimens used for the SSR tests with flowing ethanol had a gage length of 51 mm (2 inches) and a gage diameter of 4.76 mm (0.1875 inches). The longer gage length and larger gage diameter were selected to produce a more uniform flow across the gage length of the specimens (Figure 1). A displacement rate of 2×10^{-6} inches/sec was used, which produced a strain rate of 1×10^{-6} sec^{-1}. The test cell was made of one inch square carbon steel bar stock that was center bored with a 12.7 mm (0.5 inch) drill to produce the test chamber, see Figure 1. Prior to conducting the SSR tests, the internal portion of the test chamber was exposed to deionized water at room temperature for one month to produce an oxide film on the carbon steel and more closely simulate a rusted/mill scaled pipe wall. The remainder of the flow loop was fabricated of stainless steel with the exception of five-foot sections of tubing that connected to the test chamber, which were fabricated of 1010 carbon steel, to avoid undesirable galvanic effects. All of the tubing in the flow loop was 9.25 mm (0.375 inch) diameter and 0.89 mm (0.035) inch wall thickness. The reservoir had a volume of approximately 12 liters and 4 liters of ethanol was used for each test. A schematic of the flow loop is shown in Figure 2.

Specimens were tested under freely corroding conditions. The specimen and flow loop were electrically isolated from the specimen grips and test cell in the SSR test machine. The tests were performed at room temperature and the reservoir in the test loop was kept under quiescent condition. The tested scavenger was added into the reservoir to achieve the targeted dosage. The solution was recirculated through the loop for two weeks or until the oxygen concentration dropped to below 40 ppm, whichever was reached first, prior to the SSR tests. The dissolved oxygen concentration was monitored with a Polestar oxygen probe during the SSR test.

After testing, the specimens were examined and optically photographed. The fracture surfaces were examined in the SEM for indications of SCC. Other parameters that were recorded for each test included the maximum load, reduction in gage diameter of the specimen, and the time to failure.

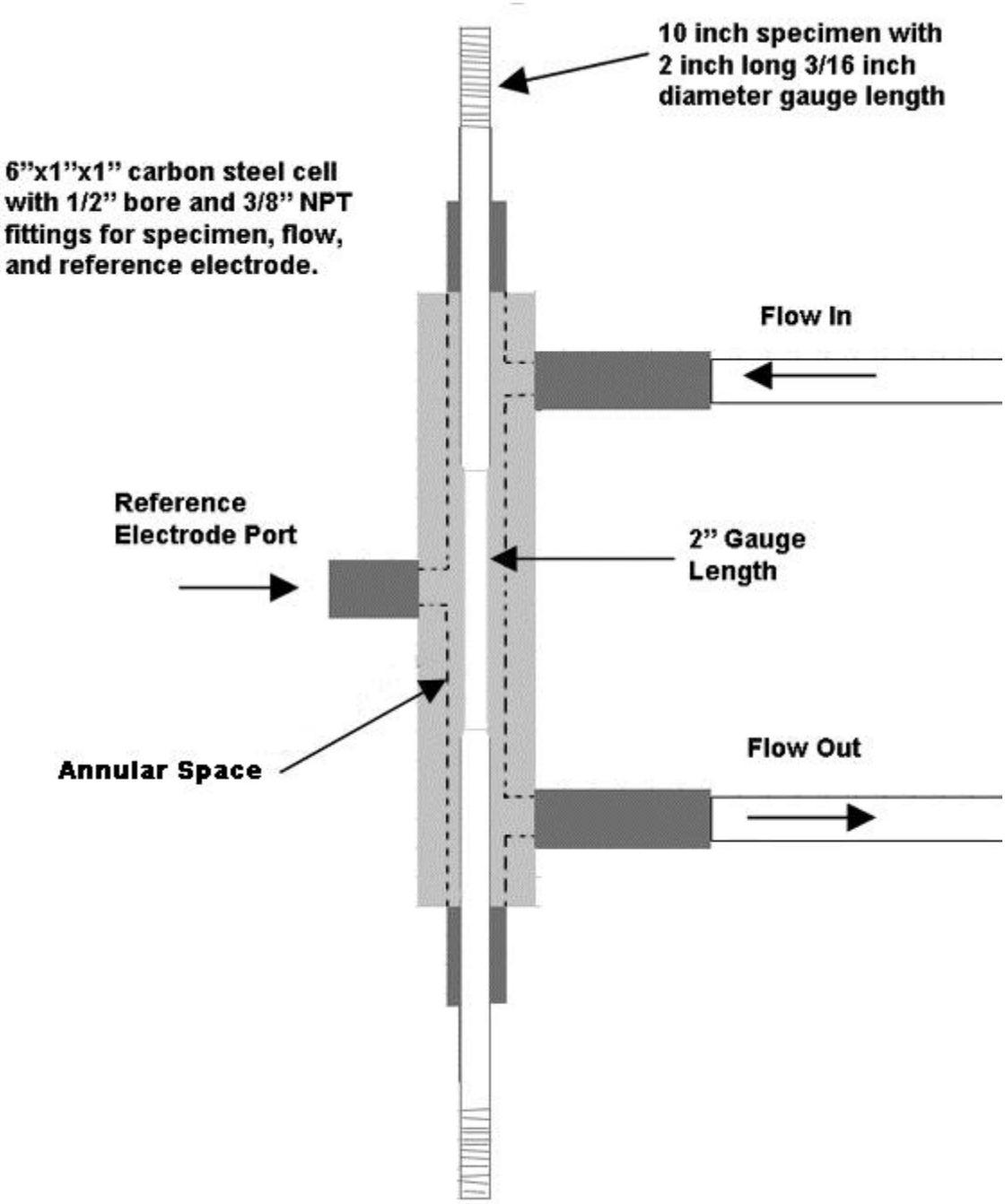


Figure 1. Drawing of test chamber and specimen used for the SSR test under flowing conditions.

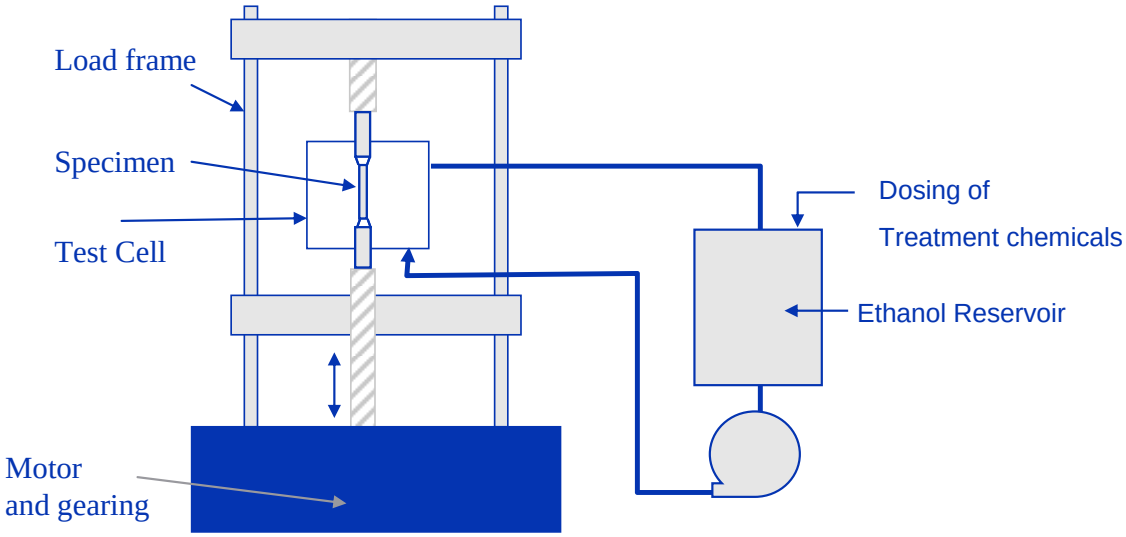


Figure 2. Schematic of flow loop used for SSR tests under flowing conditions.

4.4 Crack Growth Rate Test

A crack growth rate (CGR) test was performed to evaluate the performance of an oxygen scavenger that demonstrated the best performance in the flowing SSR tests. The test was performed on compact tension specimen (see Figure 3) under cyclic loading conditions. These load conditions are designed to simulate the loading conditions on a just- surviving crack in a pipeline that has been previously hydrostatically tested. The imposition of a cyclic load is important since it produces continuous micro-plastic deformation that enhances SCC growth and simulates the ripple load effect from pressure fluctuations on an operating pipeline. The ratio of the minimum to maximum load (R ratio) in the tests ranged from 0.6 to 0.8 and the cyclic frequency was 1.4×10^{-4} Hz (one cycle every 2.8 hours). These conditions are typical of cyclic pressure fluctuations on liquid petroleum pipelines. During the crack growth test, cracking was initiated in aerated SFGE to establish stable crack growth. The scavenger then was added to the solution with the proper amount to achieve the targeted dosage level. The crack growth was monitored as a function of time. When the slope of the crack length vs. time curve became shallower, it indicates the scavenger is in fact playing a role in prevent SCC.

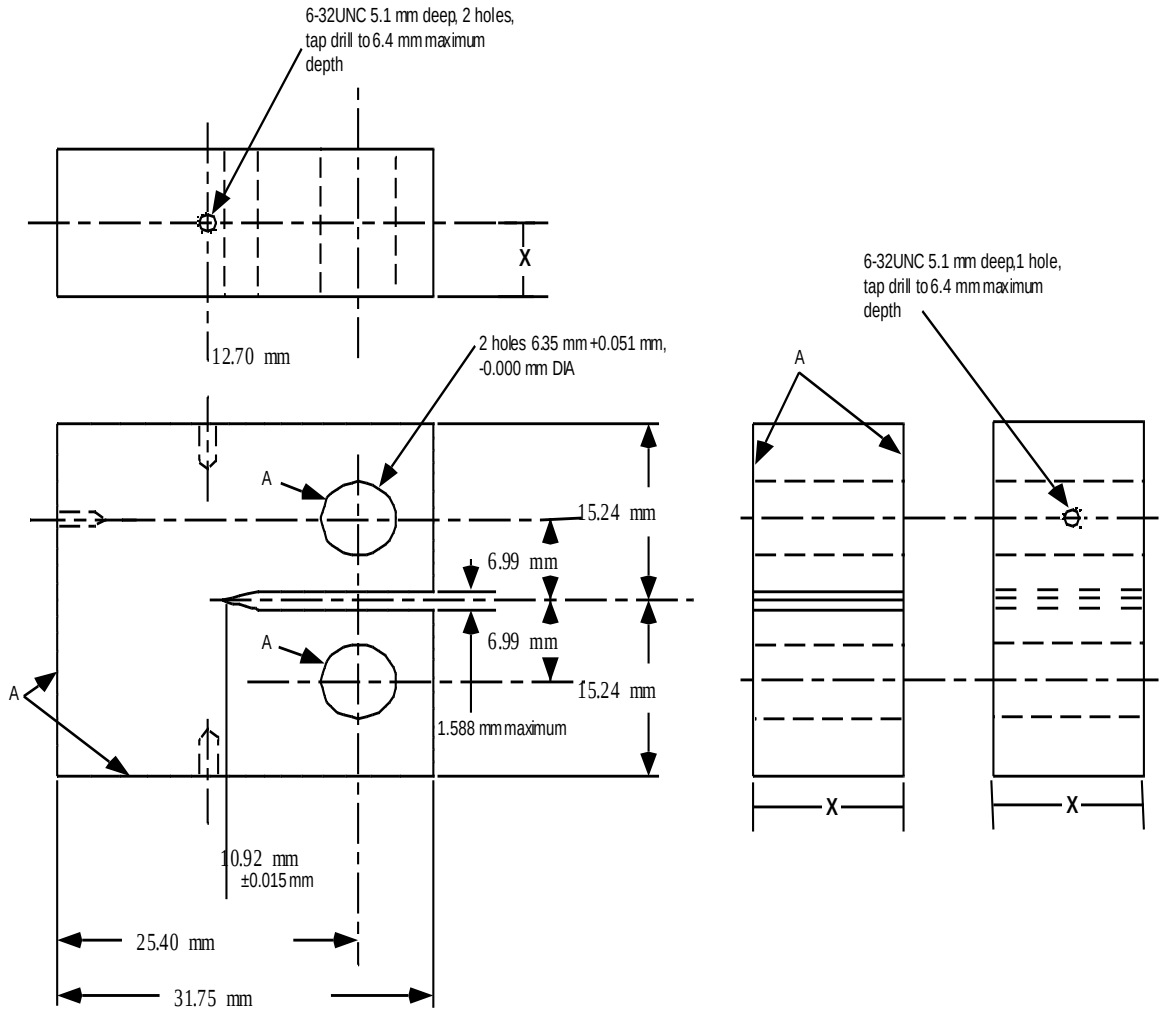


Figure 3. Schematic of compact tension specimen.

4.5 Flow Loop Test

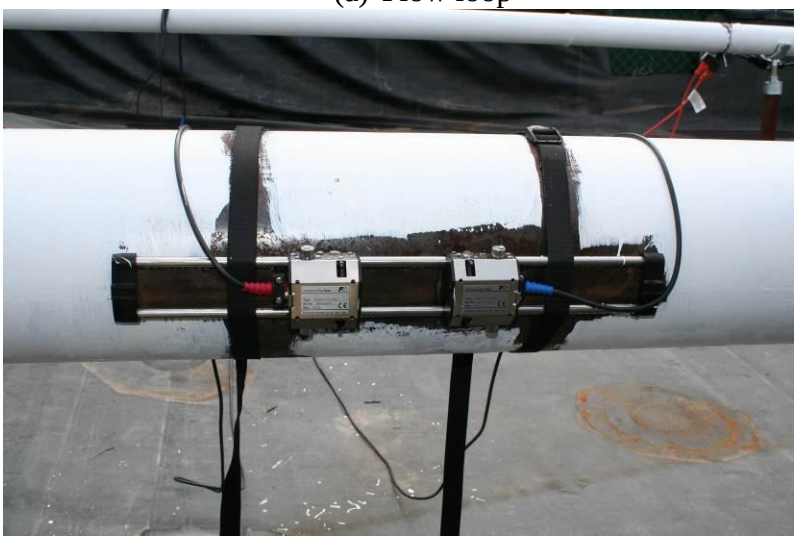
A larger scale flow loop test was performed to evaluate the following:

a. Oxygen consumption rate in the pipeline
b. Direct oxygen measurement system under flow representative of the field condition
c. Oxygen scavenger under conditions similar to those in the field

The loop dimensions were approximately 35 feet by 6 feet with a cast iron (wetted surfaces) pump and a carbon steel ambient pressure 700-gallon reservoir (Figure 4 (a)). The loop consists of pipe sections with 4 inches and 8 inches in outer diameter. The flow rates were set at 1.6 ft/s (eight inch pipe) and 6.2 ft/s (four inch pipe). These rates were monitored with ultrasonic flow

meters mounted on the pipe (Figure 4 (b)). The oxygen probe was installed in a port on the four inches pipe section (Figure 4 (c)). Three weight loss coupons were mounted on a rack and the rack was installed in a port on the eight inches pipe section. 350 gallons of FGE provide by ADM was used in the flow loop testing. After the loop was filled with FGE, it was run for two weeks without changing any conditions to establish the stable oxygen level and also to explore whether the corrosion process on the interior surface of the pipeline can decrease the oxygen concentration appreciably. After two weeks of control testing, nitrogen and oxygen scavenger were introduced at various time to evaluate the efficacy of these methods in removing oxygen. At the end of the test, the weight loss coupons were removed and examined for corrosion damage. Corrosion rates were obtained for the samples showing significant weight change.

(a) Flow loop



(b) Flow meter

(a) DSP 4000 oxygen probe

Figure 4. The flow loop for FGE testing.

4.6 Long Term Immersion Tests

The role of oxygen on the corrosion behavior of carbon steel was confirmed by long term immersion tests in SFGE with different aeration conditions. Long term weight loss experiments were set up for carbon steel 1010 coupons in E95 solution with different gas purging. The following gas mixtures were tested: pure N_2 (99.999%), 1% O_2+99% N_2, 5% O_2+95% N_2, and zero air (no CO_2). Test solutions were pre-purged with gas mixtures overnight before being transferred into the test vessel. Carbon steel coupons were ultrasonically cleaned with isopropanol, rinsed with deionized water and blow-dried with nitrogen gas. Three coupons were placed on one hanging rack made of PTFE and glass and the setup was then placed in the test vessel. The test vessel was purged with gas mixture for a minimal of two hours before solution transfer. A moisture trap was used to capture any possible water from the gas mixture. For the test vessel with pure N_2, a positive pressure of ~1 psi was maintained and monitored throughout the entire test to avoid any possible oxygen ingression from the atmosphere, as shown in Figure 5. Tests were carried out for at least one month with continuously gas purging. The gas purging rate was really slow to minimize solution loss.

Figure 5. Test setup for weight loss measurement of 1010 carbon steel coupons in SFGE with different gas purging.

4.7 Development of a Direct Oxygen Measurement System

The oxygen measurement equipment manufactured by Polestar Technologies has been demonstrated and used in other projects to measure the dissolved oxygen concentration in pure ethanol and in FGE. The probe measures the partial pressure of oxygen in the media by a proprietary fluorescent technology. Assuming the solubility of the oxygen follows Henry's Law, the measured partial pressure, after compensating for the solution vapor pressure, can be converted to concentration if the Henry's Law constant is known. This practice is generally applicable to pure ethanol since the vapor pressure for pure ethanol and the Henry's Law constant for oxygen in ethanol can be found in the literatures. For FGE, however, the following needs to be available to make it possible to directly measure the dissolved oxygen concentration:

a). vapor pressure of FGE

b). a set of equations that describe the relationship between oxygen partial pressure and concentration in FGE

An effort was undertaken to develop a set of equations that describe the relationship between oxygen partial pressure and oxygen concentration in ethanol gasoline fuel blends. The new expressions will enable direct determinations of oxygen levels in fuel using intrinsically safe

optical oxygen sensing technologies. The optical sensing technologies are based on polymer membranes that are embedded with fluorescent indicator molecules. Oxygen in the solution being monitored diffuses into the sensing membrane to yield a partial pressure in the membrane that is equal to that of the solution. The oxygen freely diffuses throughout the membrane where it encounters the fluorescent indicator in its emissive excited state resulting in a quenching reaction. The oxygen quenching reaction increases the rate of excited state deactivation resulting in a reduction in the fluorescence lifetime of the indicator.

The development of the new expressions relating partial pressure to concentration was accomplished using data from measurements of the vapor pressure and oxygen solubility of synthetic fuel blends made by mixing E0 gasoline and absolute ethanol. These data were recorded from a total of five (5) mixtures over the temperature -5 to 50^{o}C. Vapor pressure measurements were performed to account for the contribution of vapor pressure to the total system pressure of which the partial pressure of oxygen will also contribute.

Vapor pressure measurements

Vapor pressure measurements were made on a set of synthetic fuel mixtures created from a sample of E0 gasoline and absolute ethanol. A total of five (5) mixtures ranging from E5 to E95 were studied over the temperature range -5 to 50^{o}C using the ASTM D2879-97 (2007) standard method and the isoteniscope apparatus shown in the photographs of Figure 6. The system consists of a constant temperature circulating water-bath, a vacuum pump with trap, ballast tank, absolute pressure gauge, test bath and glass isoteniscope. A water/ethylene glycol solution is pumped from the water-bath and through a copper coil submerged in the test bath to control the temperature at which measurements of vapor pressure is to be made. A NTIS-traceable thermometer is used to monitor the bath temperature.

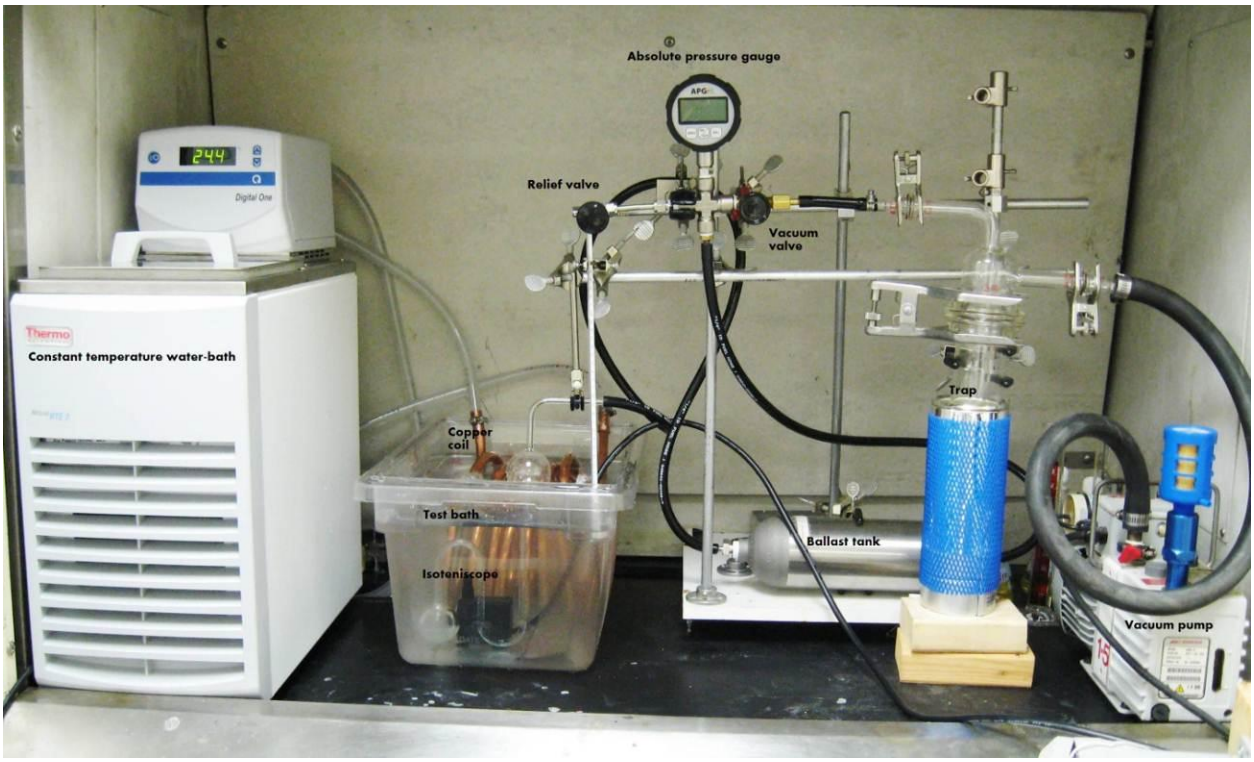


Figure 6. Photographs isoteniscope apparatus for measurements of vapor pressure.

Tests of the isoteniscope apparatus were made using n-hexane as a vapor pressure standard. Measurements of the vapor pressure for n-hexane were found to agree to within 2 mmHg with accepted values.

Work with GC determinations of oxygen concentration

The original work plan called for measuring the oxygen concentration of the synthetic fuel samples using a Hewlett-Package Model 5890 series II gas chromatograph (GC) and the tandem column method developed by Rubey et al [1][1] for measuring trace levels of oxygen in jet fuel. A GC was therefore equipped with a pair of packed fore-columns, connected in series, containing silanized diatomaceous earth followed by Porapak Q. These columns were to isolate the heavier fuel components from the permanent gases while the light hydrocarbons would be separated on a third analytical column containing a 0.5 nm molecular sieve. Detection would be achieved using a combination of thermal conductivity and flame ionization detectors. The separation and detection of oxygen is performed with helium as the carrier gas and the columns maintained at

[1] W. Rubey, R. Striebich, S. Anderson, et. al., "In Line Gas Chromatographic Measurement of Trace Oxygen and Other Dissolved Gases in Flowing High Pressure Thermally Stressed Jet Fuel", Prepr.-Am. Chem. Soc. Div. Petro. Chem, 37 (1992):p371

room temperature. The retained heavier fuel components would be removed from the isolating fore-columns following each sample test by back flushing the fore-columns at high temperature. This procedure avoids possible contamination of the analytical column which could impact dispersion of the permanent gases prior to detection. Preliminary testing of the system was conducted using room temperature air-equilibrated samples of cyclohexane and n-octane for which oxygen solubility data already exists. Several difficulties were encountered during these preliminary tests including poor resolution, repeatability, and sensitivity for the oxygen peak. A further complication of the method was the time required to completely remove the fuel components from the fore-columns in the system – often more than a half hour. After much effort and limited success, attempts were made to run tests on a synthetic fuel sample of E10 to determine if similar problems would be observed. GC runs with the E10 sample exhibited significantly greater variability with significant dispersion in the post fore-column sample traces indicating poor isolation of the permanent gases from the ethanol in the sample. As a result, the GC method was deemed to be poorly suited to the task of determining the oxygen concentration in the synthetic fuel samples.

Development of alternative oxygen measurement method

Given the difficulties encountered with the GC method of analysis, an alternative method for quantifying the oxygen concentration of fuels based on the use of fluorescence lifetime oxygen quenching was developed. Oxygen quenching of fluorescent molecules such as pyrene has previously been shown to enable direct determinations of oxygen in jet fuel over a wide range of temperatures. These measurements are based on the ability of oxygen to quench the emissive excited state of some fluorescent compounds yielding reductions in the intensity (I) and lifetime (τ) of the sample's fluorescence emission. The relationship between the oxygen level in the sample and the observed degree of fluorescence quenching is described by the Stern-Volmer kinetic expression of Equation 1, wherein I_o and τ_o are the intensity and lifetime in the absence of oxygen and K_{SV} is the Stern-Volmer constant.

$$I_o/I = \tau_o/\tau = 1 + K_{SV}[O_2] \qquad (1)$$

The use of fluorescence lifetime measurements will enable determinations of the oxygen solubility of the fuels by comparing the degree of quenching with ethanol for which the solubility of oxygen is well documented.

Fluorescence lifetime is the average time a molecule resides in its excited state prior to emission of a photon. Fluorescence lifetimes are easily measured using phase-sensitive fluorescence detection. In this process, fluorescence is excited using a sinusoidally modulated light source thus producing a sinusoidally modulated emission of the same frequency. Due to the meta stable

nature of the excited state, the fluorescence signal is phase shifted relative to that of the excite signal. The phase shift between the two signals ($\Delta\Theta$) can be used to calculate the lifetime of the fluorescence according to the expression,

$$\tau = \tan(\Delta\Theta)/2\omega \qquad (2)$$

where ω is the angular frequency of modulation.

The Stern-Volmer constant is unique to the fluorescent probe molecule and includes a geometric bimolecular quenching constant that relates to the quenching efficiency of the molecule. Tests of the degree of quenching for a probe molecule run in solvents having a known oxygen solubility can be used to determine this factor for the probe which can then be applied to other quenching data collected from the solution of interest.

Tris(diphenylphenanthroline) ruthenium chloride (dppRu) was selected as the probe molecule for the synthetic fuels work. This organo-metallic complex is highly quenched by oxygen, is soluble in ethanol/gasoline mixtures, and has a fluorescence lifetime in the microsecond timeframe making it well suited to fluorescent lifetime determinations at relatively low modulation frequencies (50kHz). Initial tests of the quenching efficiency of dppRu in ethanol have been conducted over the temperature range 0 to 50^{o}C from which the bimolecular quenching factor will be evaluated. These phase shift data were collected from dppRu doped solutions of de-oxygenated ethanol and ethanol equilibrated with a gas mixture containing 3% oxygen in nitrogen.

5.0 RESULTS

5.1 Task 1: Scavenger Performance Evaluation

5.1.1 SSR Tests Under Flowing Conditions

The results of the SSR tests are summarized in Table 1. Five oxygen scavengers were evaluated: Hydrazine, DEHA, Isoasorbic acid, Hydroquinone and MethylEthylketoxine. Note that scavengers specifically designed for use in FGE are not available and thus the above ones, used in boiling water reactors to remove oxygen, were evaluated in this work. Thus, the concentration level recommended by the manufacturers for their current application were used in this work to investigate if they are effective at the recommended dosage to prevent SCC of carbon steel in FGE. Among them, only one test was performed with Hydrazine to establish a baseline for oxygen scavengers. No further testing was performed with Hydrazine because it is toxic and is not recommended as a frequently used chemical in FGE. A test without any added scavenger was also performed to ensure that SCC can be produced under flowing and aeration conditions. When

the scavenger was used, the solution reservoir was maintained at quiescent condition (i.e., without active air sparging).

Table 1. Flowing SSR test matrix.

Test ID	Scavenger	Concentration (ppm)	Aeration	SCC (Y/N)	Final Oxygen Concentration (ppm)	Remarks
1	None	N/A	Y	Y	N/A	Control test
2	Hydrazine	1000	N	N	< 5 ppm	
3	DEHA	5200	N	N	~8 ppm	Significantly over dosed than recommendation
4	Isoasorbic acid	1760	N	Y	Pump failure	pump failure
5	Hydroquinone	2200	N	Y	80 ppm	
6	MethylEthylKetoxine	1728	N	Y	80 ppm	
7	DEHA	200	N	Y	84 ppm	
8	Isoasorbic acid	1720	N	N	44 ppm	

The appearance of the sample tested in aerated SFGE without any scavenger is shown in Figure 7. Cracks can be clearly seen on the gauge section. This confirms that the carbon steel is susceptible to SCC in the aerated SFGE under flowing conditions.

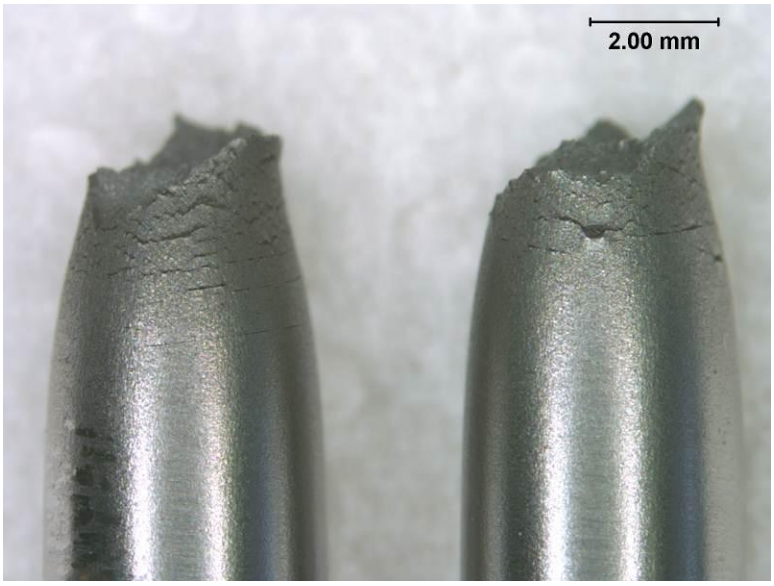


Figure 7. Optical photograph of the SSR sample tested in aerated SFGE without any scavenger under flowing condition.

Figure 8 and Figure 9 show the SSR sample after testing in flowing SFGE with 1000 ppm Hydrazine. As shown, no cracking was noted on the gauge section of the sample and the fracture surface showed the typical features of a ductile failure. Thus, Hydrazine was able to remove oxygen, as confirmed by the <5 ppm dissolved oxygen level measured at the end of the test. However, as stated above, Hydrazine is a toxic chemical and is not recommended to be used in FGE. Thus, even though it showed excellent performance in preventing SCC by consuming oxygen, no further evaluation was conducted in this work.

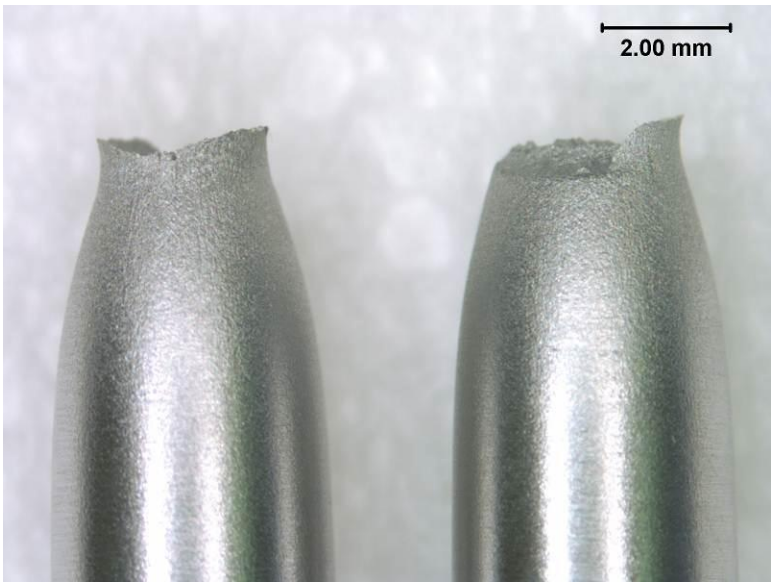


Figure 8. Optical photograph of the SSR sample tested in flowing SFGE with 1000 ppm hydrazine.

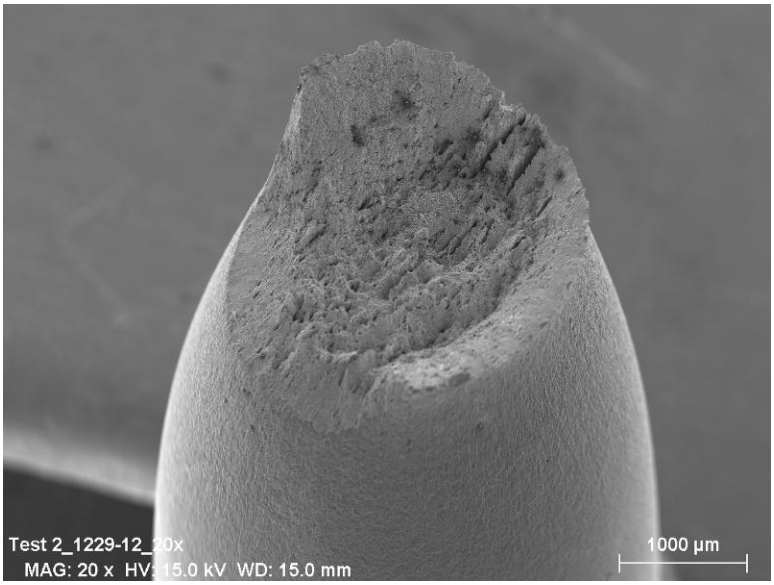


Figure 9. Electron photograph of the SSR sample tested in flowing SFGE with 1000 ppm hydrazine.

In Test 3, the DEHA was not able to decrease oxygen level at the recommended level (200 ppm) and the concentration was thus significantly increased to 5200 ppm. Although no SCC was noted on the sample with this level of oxygen scavenger, such a high oxygen scavenger dosage may cause other issues with downstream material. Thus, another test was performed (Test 7) with the

recommended dosage at 200 ppm. The post tested sample appearance is show in Figure 10. Secondary cracks were observed on the sample. This suggests that the DEHA at 200 ppm is not able to prevent SCC. This is likely because DEHA, at this concentration, cannot remove the dissolved oxygen as the measured oxygen level at the end of the test was still >80 ppm.

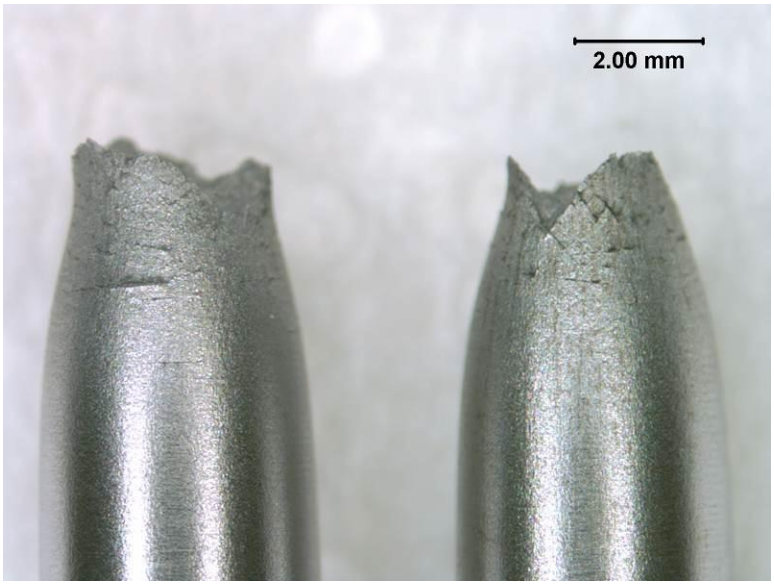


Figure 10. Optical photograph of the SSR sample tested in flowing SFGE with 200 ppm DEHA.

A pump failure occurred in Test 4 and thus the evaluation of isoascorbic acid was repeated in Test 8. The post tested SSR sample is shown in Figure 11. No cracking was noted on the sample. The fracture surface showed the feature of typical ductile failure. The dissolved oxygen concentration at the end of the test was about 40 ppm, half of the saturation oxygen level in FGE. This dissolved oxygen level corresponds to 10% (volume) oxygen concentration in the gas phase. The obtained results seem to suggest that the crucial oxygen level in the gas phase is higher than 10%. Alternatively, the isoascorbic acid may be providing some inhibitory effect for SCC.

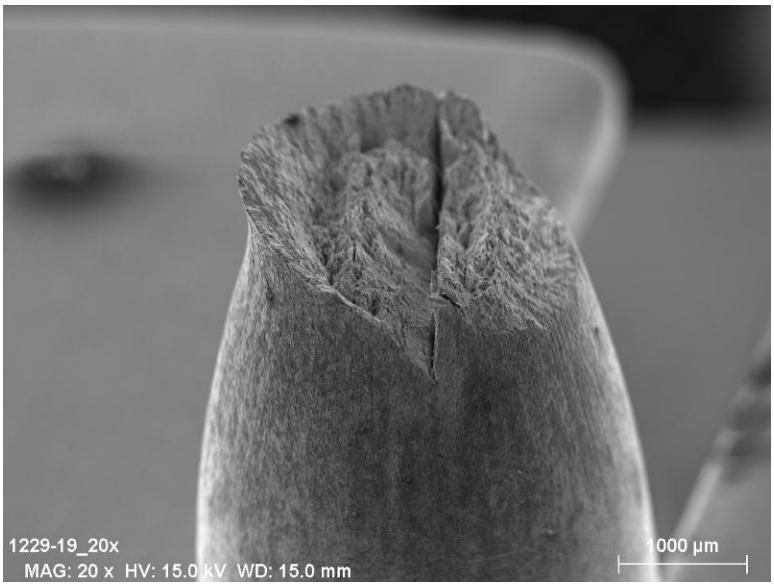


Figure 11. Electron photograph of the SSR sample tested in flowing SFGE with 1720 ppm isoasorbic acid.

Figure 12 and Figure 13 show the appearance of the samples following testing in flowing SFGE with 2200 ppm hydroquinone and 1728 ppm Methylethylketoxine, respectively. Secondary cracks are clearly evident on the gauge section of the specimens, suggesting these two chemicals were not able to consume oxygen below the critical level for SCC to occur. This is consistent with the high measured dissolved oxygen concentration (>=80 ppm) at the end of tests, as shown in Table 1.

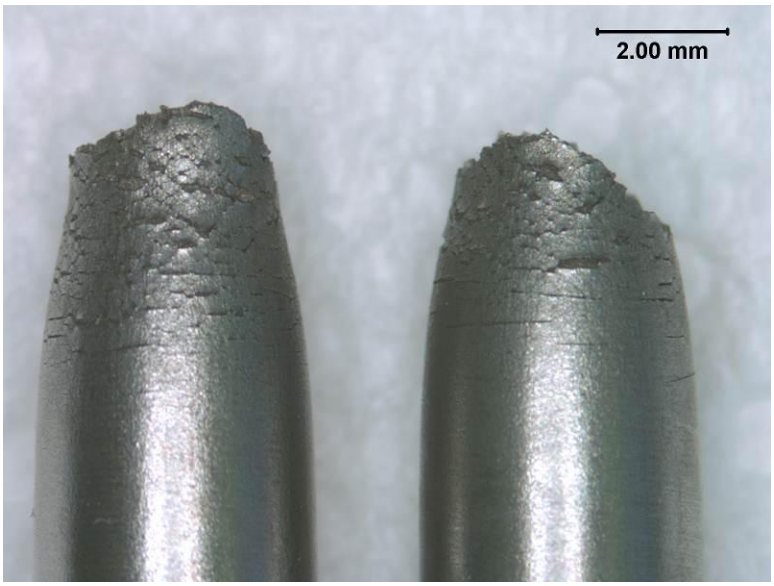


Figure 12. Optical photograph of the SSR sample tested in flowing SFGE with 2200 ppm hydroquinone.

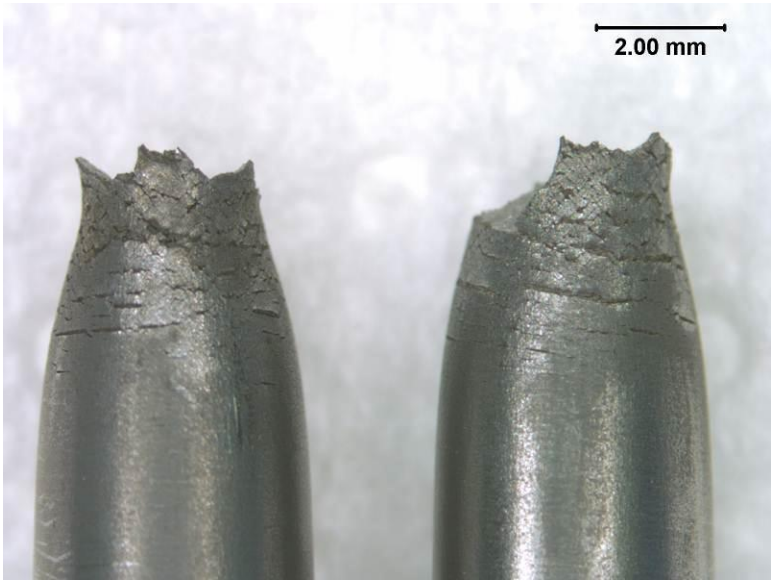


Figure 13. Optical photograph of the SSR sample tested in flowing SFGE with 1728 ppm Methylethylketoxine.

Based on the results described above, isoasorbic acid showed the best performance, taking into consideration the ability of preventing SCC and the necessary dosage. Thus, it was considered as

the most promising scavenger and was further evaluated in the CGR and large scale flow loop test. The results of these further evaluations are described in Sections 4.1.2 and 4.1.3.

5.1.2 Crack Growth Rate Test

Figure 14 shows the crack length as a function of time in the crack growth rate test that evaluated the performance of isoascorbic acid as the oxygen scavenger. Prior to the addition of the scavenger, stable crack growth was established in aerated SFGE (1.15 mm/y). The scavenger was added at a concentration of 880 ppm on Day 882. This concentration was used because it was shown in SSR tests that a concentration of 1760 ppm could in fact prevent SCC from occurring. Thus, it is worth evaluating if lower dosage can still be effective in preventing SCC.

From the results, it can be clearly seen that the slope of the crack length vs. time curve (crack growth rate) changed after the scavenger was added. This suggests that the scavenger at half of the concentration used in the SSR test was able to mitigate SCC.

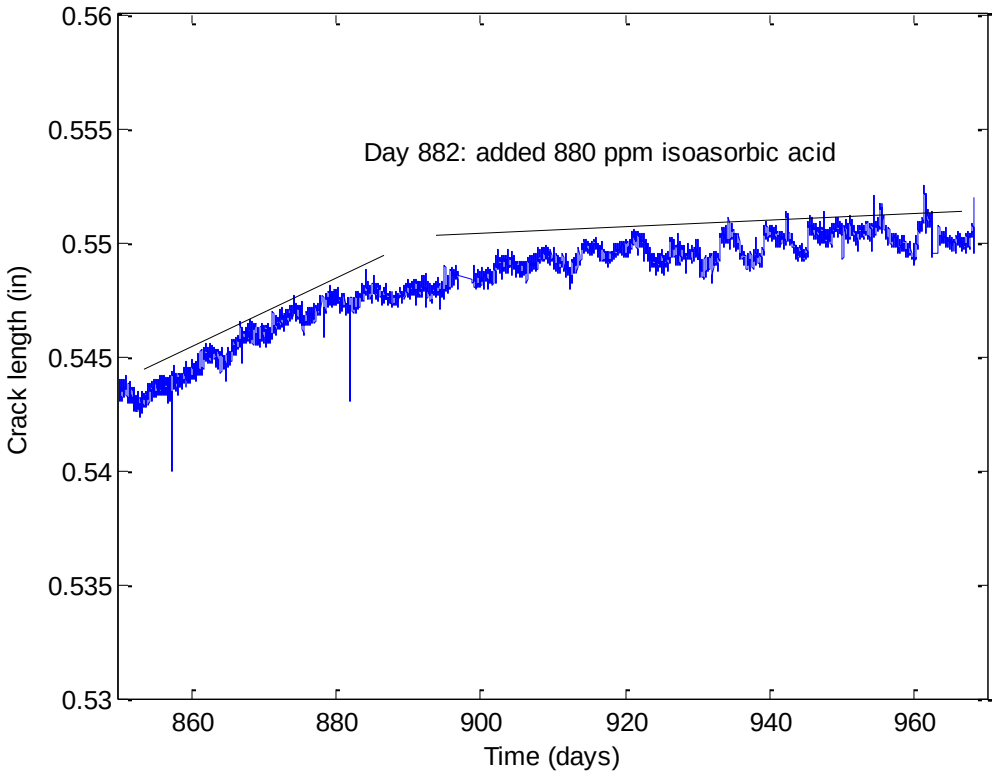


Figure 14. Crack length as a function of time before and after adding 880 ppm isoasorbic acid.

5.1.3 Flow Loop Test Results

Although the scavenger performance in preventing SCC has been demonstrated above with small scale testing, it is necessary to gain some ideas on its performance under conditions more similar to the field operations. The flow loop test serves this purpose. In addition, the direct oxygen measurement system was installed in the loop to evaluate whether it can detect the changes in the oxygen concentration when the conditions in the loop changed.

Figure 15 is the oxygen concentration measured with the installed oxygen probe as a function of time. The scavenger was not added in the first 15 days so that a baseline concentration could be established. This also can provide insights in the natural consumption of the oxygen in the FGE by corrosion process. With the rate used in the eight inches pipe, the flowing of the solution in the loop for 15 days corresponds to a travel distance of approximately 390 miles. As can be seen, the dissolved oxygen concentration did not decrease at all in the first 15 days. The reservoir tank was then sparged with nitrogen to decrease the dissolved oxygen concentration to ~40 ppm, a level that has be observed in the storage tanks based on the monitoring results obtained in a PHMSA funded project [*]. The loop was run with ~40 ppm dissolved oxygen for 27 days to explore if the oxygen can decrease from corrosion process. It can be noted that the oxygen stay relatively stable for these 27 days suggesting natural consumption is minimal. On Day 42, a concentration of 880 ppm isoascorbic acid was added and the oxygen concentration started to decay slowly and reached approximately 7 ppm on Day 71. This observation indicates that the oxygen scavenger was able to remove oxygen in the flow loop conditions that were more similar to the field operation conditions compared with those in the lab evaluation.

The reservoir tank was sparged with compressed air to increase the dissolved oxygen concentration to ~80 ppm. It was sparged with nitrogen on Day 78 to evaluate if deaeration by nitrogen is effective in removing oxygen. As shown, the oxygen concentration decreased rapidly after the tank was sparged with nitrogen, a much faster process compared with when scavenger was used. It took only a few days with nitrogen to decrease the dissolved oxygen below 10 ppm; whereas, the time it took the scavenger to decrease the dissolved oxygen to the same level was near a month. The deaeration was repeated on Day 82 to get a more accurate consumption volume of nitrogen and on Day 113 to check the performance of the oxygen probe. On Day 96, the scavenger, at 880 ppm, was added again to explore if it is effective when the initial oxygen concentration is near saturation level. It was found that the oxygen decreased much slower than when the initial oxygen concentration was 40 ppm, indicating a longer time may be needed to drop the dissolved concentration to a level below the threshold to prevent SCC.

[*] Narasi Sridhar, “Monitoring Conditions Leading to SCC/Corrosion of Carbon Steel”, PHMSA Project WP237 Report, 2010

Because it has been demonstrated in several other projects that nitrogen deaeration is effective, the measured decrease in the oxygen with the installed oxygen probe confirmed its performance as a direct oxygen measurement system.

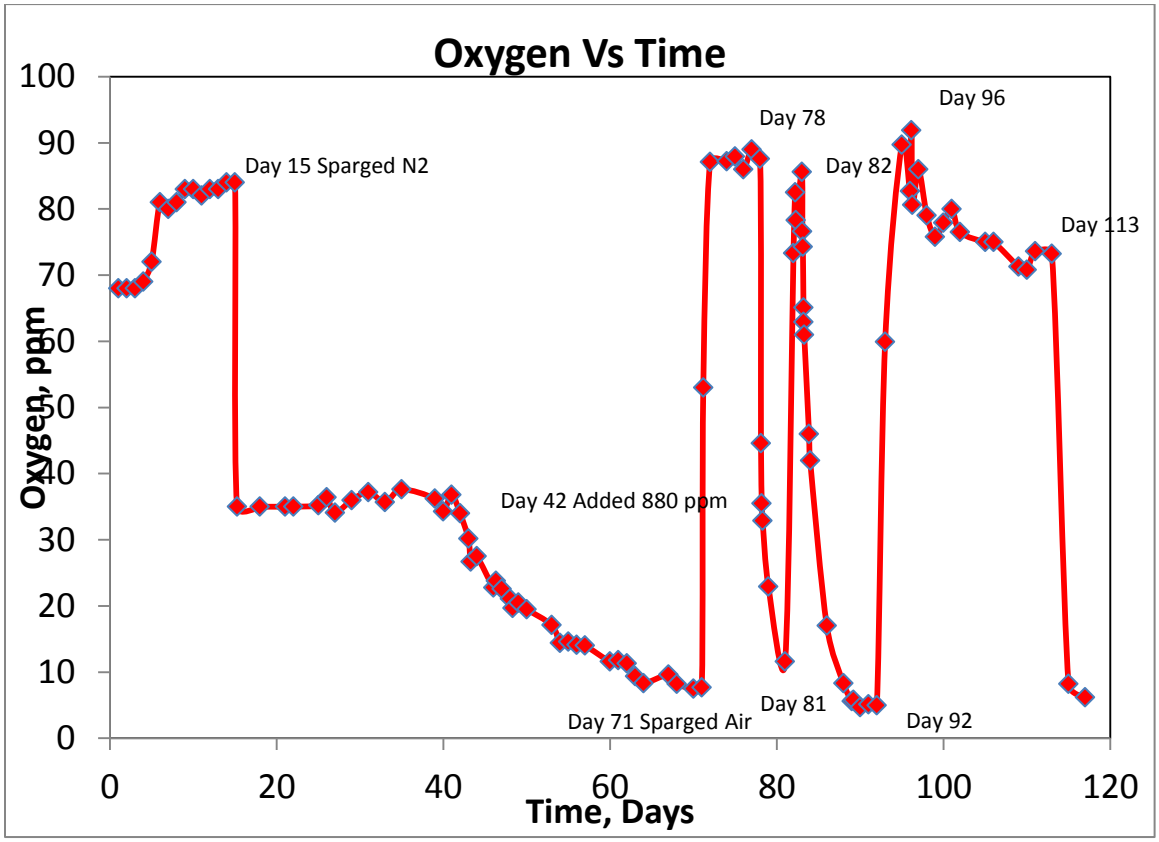


Figure 15. Measured dissolved oxygen concentration as a function of time in the flow loop test. The reservoir tank was sparged with nitrogen on Day 78, 82, 113 and with compressed air on Day 81 and 92.

Three weight loss coupons were installed in the loop to gather data on the corrosion rate of carbon steel in FGE. The corrosion rates are summarized in Table 2. The samples showed minimal corrosion rates (<0.1 mpy). This is consistent with the observation that the oxygen concentration did not decrease through corrosion process as it would take a substantial amount of time to consume appreciable amounts of oxygen via corrosion based on the obtained corrosion rates.

Table 2. Weight loss and corrosion rate of the coupons installed in the flow loop.

Coupon	Starting Weight (g)	Ending Weight (g)	Weight Loss (g)	Corrosion Rate (mpy)
1	16.6186	16.6159	0.0027	0.048533135

2	16.9270	16.9246	0.0024	0.042895725
3	16.9322	16.9293	0.0029	0.051773568

5.2 Task 2: Oxygen Transport in Pipeline

In the presence of oxygen, the corrosion of carbon steel in FGE typically is supported by the oxygen reduction reaction thereby consuming oxygen. Since the interior surface of pipelines is typically not coated, the oxygen in the FGE lots being transported through the steel pipelines is expected to be consumed by the steel corrosion process. The oxygen concentration in the transported FGE, thus, will decrease over time and along the length of the pipeline if the corrosion rate of the pipe steel is substantial.

The corrosion rates measured in the flow loop test summarized above indicate that the corrosion rate of carbon steel in FGE in the presence of oxygen is minimal. This is because oxygen in FGE promotes passivity of carbon steel. As shown in Figure 16, the presence of oxygen in SFGE had effects on OCP, repassivation potential and the passive current density of carbon steel. This behavior is different from that of carbon steel in most aqueous solutions in which oxygen typically only affects OCP.

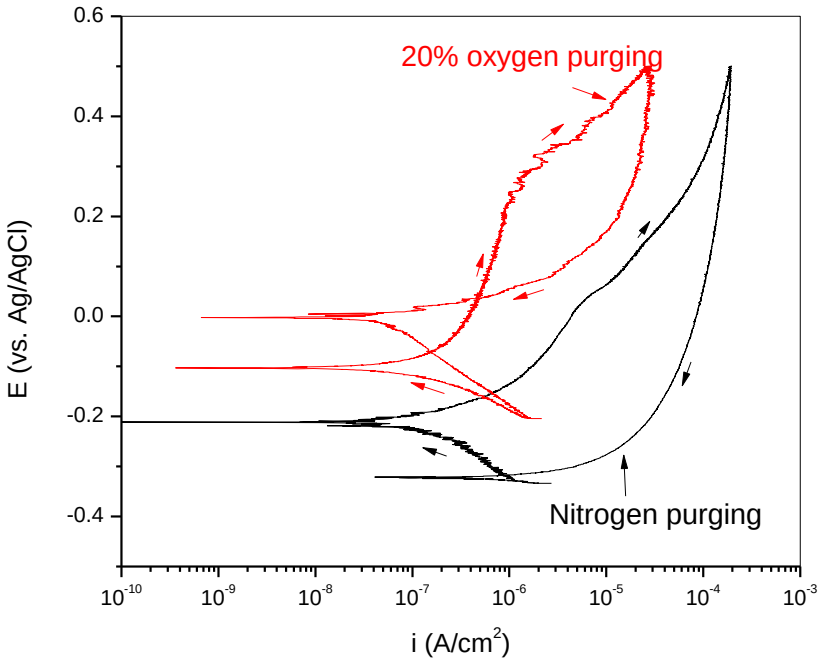


Figure 16. Comparison of potentiodynamic polarization curve obtained for carbon steel in SFGE under deaerated and aerated conditions*.

The role of oxygen on the corrosion behavior of carbon steel also was confirmed by long term immersion tests in SFGE with different aeration conditions. Figure 17 is the comparison of solutions with different sparging gas after one month of coupon exposure. A darker color indicates more dissolved iron and thus a higher corrosion rate. Corrosion was most severe with pure nitrogen purging and least severe with zero air purging. However, it appears that the weight loss was negligible, even with pure N_2 purging. Therefore, the iron concentration in each solution was analyzed by an independent laboratory and the corrosion rate was calculated based on the results. The corrosion rates are compared in Figure 18.

* F. Gui, N. Sridhar, and J. A. Beavers, "Localized corrosion of carbon steel and its implications on the mechanism and inhibition of stress corrosion cracking in fuel-grade ethanol", Corrosion, v66, 12 (2010):p125001-1

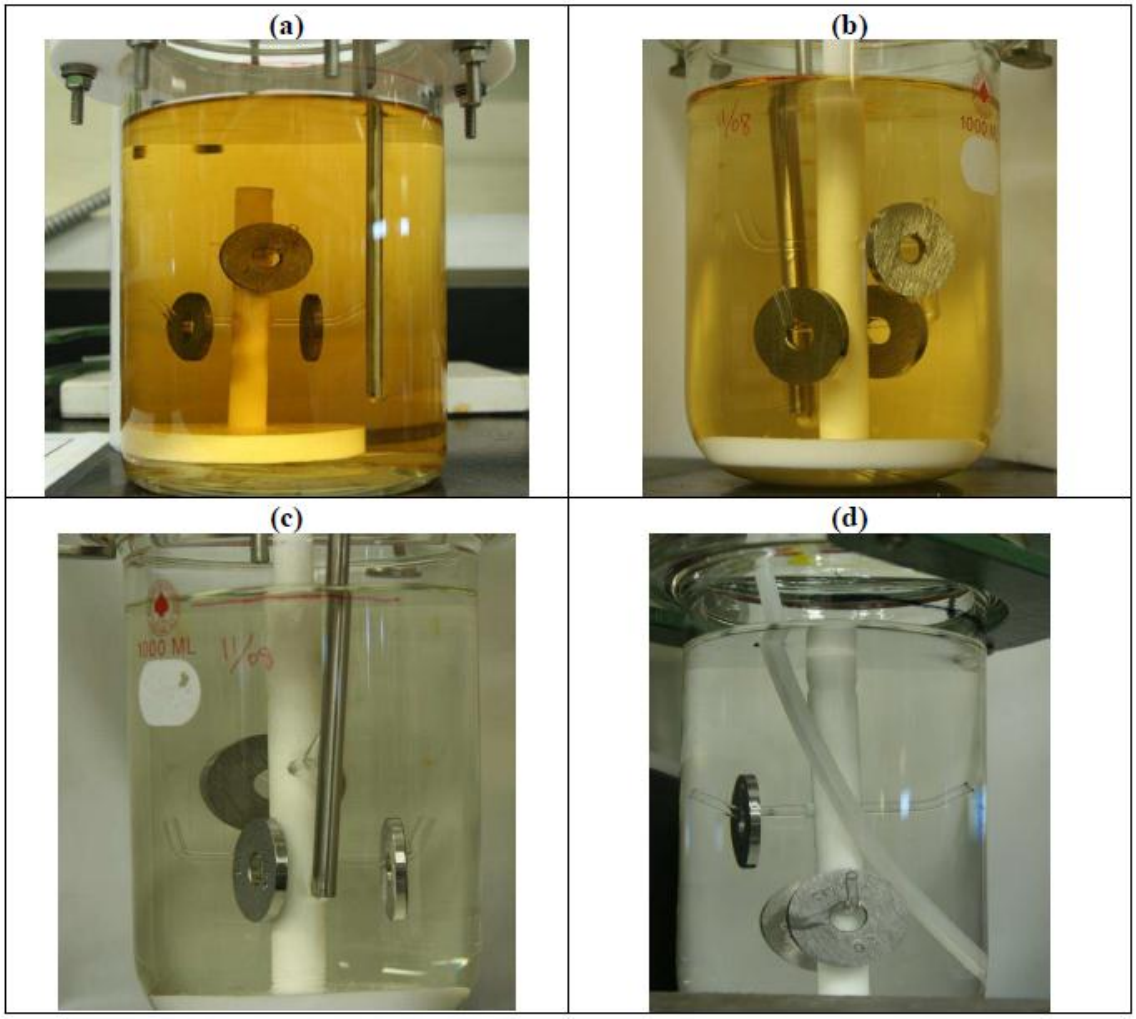


Figure 17. Final appearance of weight loss experiment of 1010 carbon steel coupons in synthetic fuel grade ethanol E95 with different gas purging: (a) pure N_2, (b) 1% O_2+99% N_2, (c) 5% O_2+95% N_2, and (d) zero air (no CO_2).

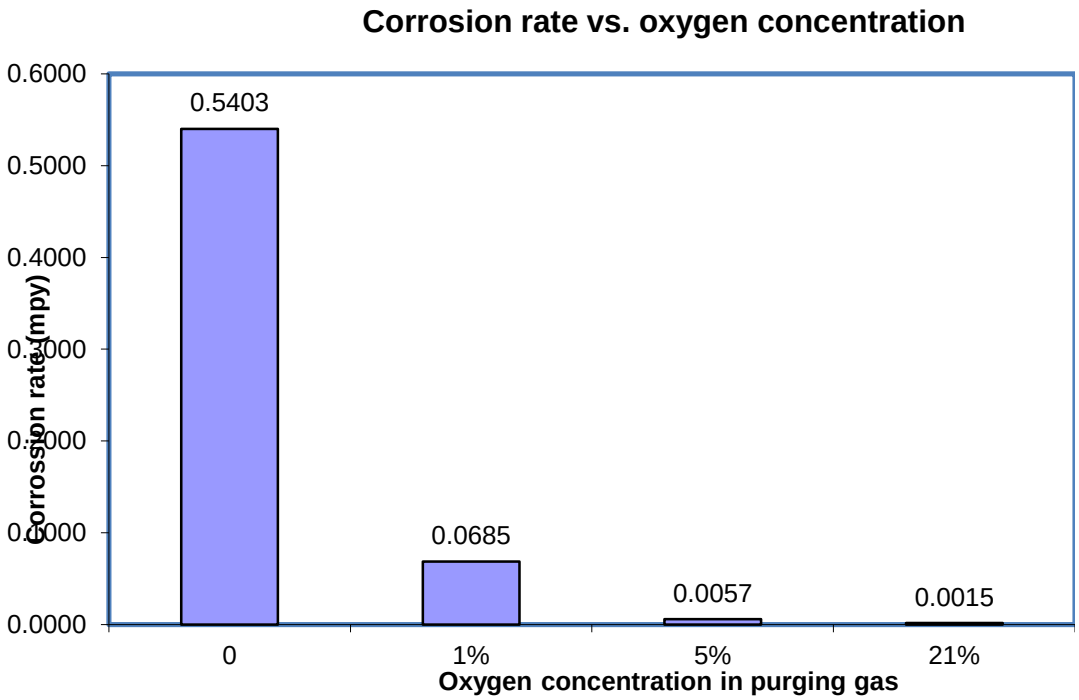


Figure 18. Comparison of corrosion rates of carbon steel in SFGE as a function of oxygen concentration in the purging gas.

The efforts described below were taken to investigate whether the small corrosion rate of carbon steel can cause substantial consumption of oxygen by corrosion.

Oxygen consumption by corrosion

If a uniform passive dissolution (anodic) current is assumed to control the corrosion of carbon steel pipes in FGE, the consumption of oxygen can be calculated by the following equation*:

$$-dC_o(x)(mol/cm^3) = \frac{j_{\lim} \cdot s \cdot A}{n \cdot F \cdot v} \cdot dx \qquad \text{Eq. (1)}$$

Where $j_{\lim}$ is the limiting current by dissolution through a passive film, s is the specific area, A is cross-sectional area and v is the volumetric flow rate. For a pipe with an internal diameter of d, $s \cdot A = \pi \cdot d$.

This equation can be further written as

* A. J. Bard and L. R. Faulkner, "*Electrochemical Methods, Fundamentals and Applications*", John Wiley & Sons, Inc.

$$C_0(x) = C_0(0) - \frac{j_{\lim} \cdot \pi \cdot d}{n \cdot F \cdot v} \cdot x \qquad \text{Eq. (2)}$$

In this equation,

$j_{\lim} = 10^{-8} A/cm^2$

$d = 10cm$

$n = 4$

$F = 96485C/mol$

$v = 0.25 \cdot \pi \cdot d^2 \cdot U = 39270 \ \ cm^3/s$, for 5 m/s flow rate

Substituting all the parameters into Eq. (20), $C_0(x)(ppm) = 80 - 6.6 \cdot 10^{-8} \cdot x(m)$

If the corrosion current is assumed to be 1 μA/cm^2 (0.45 mpy), it will take approximately 100 km (66 miles) distance for oxygen to decrease by 1 ppm, and 8,000 km (5000 miles) for the complete consumption of 80 ppm oxygen due to the linear dependency. For the corrosion rate experienced in the aeration condition, the distance that is needed to consume the oxygen would be substantially higher.

Therefore, it is not realistic to rely on an oxygen concentration decrease by the corrosion process as an SCC mitigation method. The flow loop test results have provided some evidence. Without deaeration or using an oxygen scavenger, the oxygen concentration is not expected to change appreciably in the pipeline with time since the corrosion consumption rate is minimal. Thus, it is important to understand if oxygen uptake occurs in a pipeline which is transporting FGE that only contains a small level of oxygen, the introduced oxygen will be transported with the FGE flow to downstream pipeline without substantial concentration decay.

5.3 Task 3: Development of Direct Oxygen Measurement System

A complete set of vapor pressure data were collected from the five (5) mixtures. Empirical fits of the vapor pressure data have been made and the fit expressions documented. A plot of the results for a sample of E95 and a fit of the data are provided in Figure 19.

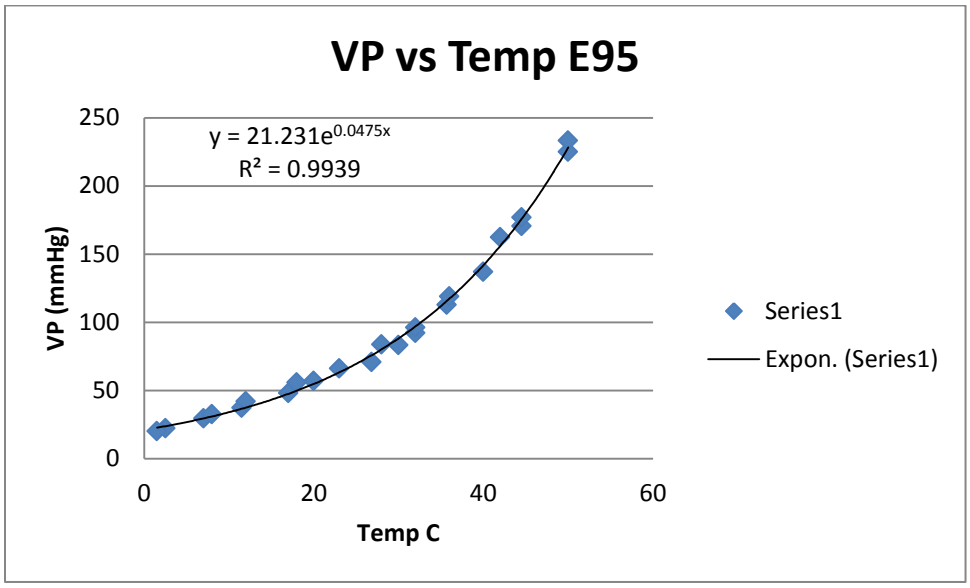


Figure 19. Graph of vapor pressure versus temperature for synthetic E95 fuel.

Determinations of oxygen concentration versus partial pressure

Quenching data were collected from samples of synthetic fuels doped with the same trace amount of dppRu using the nitrogen and 3% oxygen gas mixtures. The vapor pressure for each fuel sample was calculated at each test temperature using the fit expressions developed from the data acquired with the isoteniscope apparatus and the value used to calculate the partial pressure of oxygen in the sample ($PO_{2,HF}$). The fluorescence lifetimes of the dppRu probe was calculated using equation 2 and the degree of quenching compared with that observed with the pure ethanol samples to allow the oxygen concentration of oxygen in the hybrid fuels ($[O_2]_{HF}$) to be calculated from the expression;

$$[O_2]_{HF}\ (ppm) = [O_2]_{EtOH} * \{(\tau_o/\tau)_{HF}/(\tau_o/\tau)_{EtOH}\} * (PO_{2,HF}/PO_{2,EtOH}). \quad (3)$$

A sample data set is provided in Table 3.

Table 3. Data from oxygen quenching test involving E95.

Temp	$Phase_{3\%}$ (deg.)	$Phase_{N2}$ (deg.)	VP_E95	PO_2 (mmHg)	Tau_{N2} (sec.)	$Tau_{3\%}$ (sec.)
4.9	23.04	54.07	26.7	21.9	4.39E-06	1.35E-06
12.4	22.03	52.15	38.2	21.6	4.09E-06	1.28E-06
20.2	20.27	49.53	55.4	21.1	3.73E-06	1.17E-06
27.2	20.23	46.65	77.2	20.4	3.37E-06	1.17E-06
34.8	19.43	42.93	110.8	19.4	2.96E-06	1.12E-06
45.8	18.42	36.49	186.9	17.1	2.35E-06	1.06E-06

DSP4000 Code Modification

Vapor pressure and oxygen solubility measurements were made on synthetic fuel mixtures created from a sample of E0 gasoline and absolute ethanol. A total of five (5) mixtures ranging from E5 to E95 were studied over the temperature range -5 to 50°C. Data from these studies were compiled and a set of expressions generated that could be used to convert optical readings of oxygen partial pressure (PO_2) to oxygen concentration.

Empirical fits of plots of oxygen concentration versus partial pressure were developed for each of the fuel samples. These fits required different types of expressions depending on the composition of the fuel mixture thus precluding the development of a single expression that could be used to convert PO_2 readings to concentration over the full range of potential fuel formulations. In light of this, unique versions of the system code used with Polestar's DSP4000 optical oxygen monitor were drafted for each of the five (5) evaluated fuel mixtures. The various versions of the code can be loaded into the DSP4000 via a USB Flash Drive that plugs into the DSP4000 allowing users to select the specific code for the type of fuel to be monitored.

DSP4000 Laboratory Evaluation

The DSP4000 was evaluated at DNV to directly measure oxygen concentration in SFGE and several FGE solutions saturated by 21% oxygen (in breathing air). The results are summarized below:

Solution	O2 ppm Range	Temp C	Pressure
SFGE	76.3 – 77.4	20.7	14.7
1602553	76.3 – 77.3	19.8	14.7
1524407	76.2 - 77.6	19.9	14.7

The measured values were close to the theoretical value of oxygen saturation concentration in FGE.

5.4 Task 4: Feasibility Evaluation

These factors are considered in evaluating the feasibility of oxygen control as a method to prevent carbon steel SCC in FGE:

1. Technical feasibility
2. Cost
3. Feasibility to implement in field
4. Possible impact to downstream user

The results obtained in this work have shown that both deaeration and oxygen scavengers can be used to mitigate SCC. In the flow loop test, both methods were able to remove oxygen from FGE although it took up to one month for the oxygen scavenger to decrease the oxygen concentration to below 10 ppm from an initial oxygen concentration of ~40 ppm. The oxygen scavenger, however, would need more reaction time to remove the oxygen from an initial concentration of 80 ppm to below 40 ppm (could be several months), which appears to be below the critical concentration for SCC initiation based on the SSR test results.

When implementing these methods in the field, it is important to select a cost effective method. The cost for isoascorbic acid is $200/Kg. Thus, the chemical needed (at a concentration of 880 ppm) for an ethanol storage tank with 29000 barrels ethanol would be approximately 4976 Kg, corresponding to a chemical cost of approximately $995K. Assuming bulk chemical will only cost $100/Kg, the chemical will still cost about $50K, not to mention the cost involved in the operation when the scavenger is added. If nitrogen is used, the investment on materials will be

much less (~$9000) because of its low cost ($10/tank and half tank to change the oxygen concentration for 7 barrels FGE to 40 ppm). However, infrastructure investment is required to construct compress nitrogen storage tanks as well as necessary supplying pipes near the storage tanks and the entry point of a pipeline. Moreover, the deaeration procedure needs to be optimized to reduce the time needed to remove the oxygen from either storage tanks or the batch ethanol that will be transported by a pipeline. For instance, a calculation shows that if only the head space in a storage tank full with ethanol is deaerated it would take 1x10 seconds (more than 300 years) to change the concentration from 80 ppm to 40 ppm assuming no agitation in the solution. That is, oxygen transporation through ethanol is controlled by the diffusion process with a diffusivity of $2x10^{-5}$ cm^2/s.

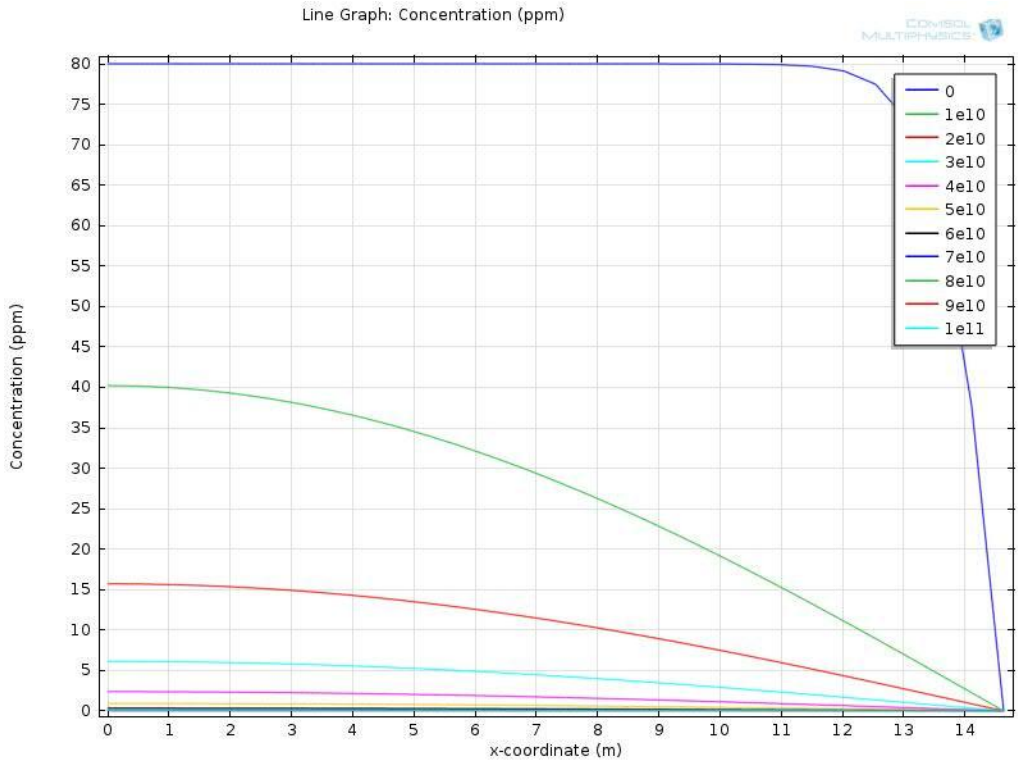


Figure 20. Oxygen concentration change in a storage tank (14.5 m ethanol depth) with the tank head space remained at zero oxygen.

If proper agitation method in the storage tank can be implemented to reduce the time needed to remove oxygen, nitrogen deaeration would be a better option in removing oxygen to prevent SCC from the view point of the end users since no chemical will be added in the FGE. The impact of scavengers on materials in the engine could be a concern when oxygen scavengers are

used. Detail engine material compatibility testing needs to be carried out to draw definitive conclusions on the scavenger effect on downstream materials.

Corrosion aspects need to be considered as well. As shown earlier, carbon steel corrodes in FGE at a higher rate in deaerated condition compared to aerated condition (0.5 mpy vs. 0.0015 mpy). Thus, fully deaerated FGE could cause more uniform corrosion in the pipeline, in general, although may not be as high as the lab results due to the protection from the scale. The uniform corrosion of carbon steel is substantially inhibited by the oxygen at the critical oxygen level for SCC, which is likely around 40 ppm. Therefore, the target of oxygen control should not be to achieve a deaerated condition in FGE. Rather, high oxygen concentration in FGE, while still below the critical level for SCC, would be beneficial towards reducing the corrosion rate of pipe steel in FGE.

6.0 SUMMARY

- Isoascorbic acid and hydrazine showed promising performance in preventing SCC of carbon steel in FGE by consuming oxygen. The results suggest the critical dissolved oxygen concentration for SCC to occur could be at or higher than 40 ppm (10% volume in gas phase). Hydrazine, however, was not selected as the recommended scavenger due to its toxic nature;

- The performance of the oxygen scavenger, isoascorbic acid, was confirmed in a flow loop test. While it is efficient in decreasing the dissolved oxygen concentration from an initial level of 40 ppm to below 10 ppm, it can take substantially long time to decrease oxygen concentration from an initial level of 80 ppm to below 40 ppm;

- A direct oxygen measurement system was developed that can provide the direct oxygen concentration level in FGE. The system accounts for the vapor pressure of FGE and has the equation for converting oxygen partial pressure to concentration reading embedded. The lab evaluation and the flow loop testing both confirmed its performance;

- Oxygen consumption by corrosion was proved to be minimal. Thus, measures need to be taken in pipeline operation to avoid oxygen uptake during transmission.

- The comprehensive evaluation of the oxygen control methods taking into consideration of technical feasibility, cost, field implementation feasibility and corrosion suggest oxygen control may not be an attractive method to prevent SCC for large volumes of FGE; for small volumes of FGE with proper agitation, nitrogen deaeration could be an option since it does not require the addition of chemicals and thus will not cause concerns over downstream materials compatibility;

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